ON THE ETHOCROTONIC ACID

AND THE

Mono- and Dibromdiethacetic ACIDS.

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It is with pleasure that I take this opportunity of acknowledging my indebtedness to my highly respected instructor, for the advice and counsel with which he was ever ready to aid me during the entire investigation.

ON THE ETHOCROTONIC ACID

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In the year 1863, Frankland and Duppa[1] published an account of an interesting reaction, by means of which they obtained a substance which they at first considered to be leucic either, but which was afterwards proved to be an isomeric compound, and not identical with leucic ether. The product obtained by the action of zinc ethyl on oxalic ether was decomposed with water, and as main product, they obtained by distillation an oily substance mixed with alcohol and water in the distillate, namely, leucic ether.

The reaction takes place in two phases, which they expressed in the following formulæ:

$$C^2\begin{cases} O \\ O \\ C^2H^5O \\ C^2H^5O \end{cases} + Zn^2\begin{cases} C^2H^5 \\ C^2H^5 \end{cases} = C^2\begin{cases} C^2H^5 \\ C^2H^5 \\ O \\ ZnO \\ C^2H^5O \end{cases} + \begin{matrix} Zn \\ C^2H^5 \end{matrix}\Big\} O$$

Oxalic ether. Zinco-leucic ether. Zinc ethylate.

On treating the zinco-leucic ether with water, the following decomposition takes place:

1 Liebig's Annalen, cxxvi, p. 109.

$$C^2\begin{cases} C^2H^5 \\ C^2H^5 \\ O \\ ZnO \\ C^2H^5O \end{cases} + \left.\begin{matrix} H \\ H \end{matrix}\right\} O = C^2\begin{cases} C^2H^5 \\ C^2H^5 \\ O \\ HO \\ C^2H^5O \end{cases} + \left.\begin{matrix} Zn \\ H \end{matrix}\right\} O$$

(In the above formulæ, zinc is considered as univalent.)

The process was afterwards simplified,[1] as they found it was not necessary to prepare the zinc ethyl first, but that the reaction took place just as readily on substituting ethylic iodide and metallic zinc in place of zinc ethyl.

Subsequent investigations[2] on the reaction between zinc ethyl and leucic ether led to a different hypothesis concerning the formation of the leucic ether. Zinc ethyl and leucic ether were brought together in weighed quantities, and the escaping gas was also collected and weighed. The reaction was found to take place according to the following equation:

$$C^2\begin{cases} (C^2H^5)^2 \\ OH \\ O \\ C^2H^5O \end{cases} + Zn\left\{\begin{matrix} C^2H^5 \\ C^2H^5 \end{matrix}\right. = C^2\begin{cases} (C^2H^5)^2 \\ OZnC^2H^5 \\ O \\ OC^2H^5 \end{cases} + \left.\begin{matrix} C^2H^5 \\ H \end{matrix}\right\}$$

Leucic ether. Zinco-monethyl-leucic ether.

The zinco-monethyl-leucic ether is a colorless, tenacious solid, which readily absorbs oxygen, and in contact with water is immediately decomposed according to the following equation:

$$C^2\begin{cases} (C^2H^5)^2 \\ OZnC^2H^5 \\ O \\ OC^2H^5 \end{cases} + 2H^2O = C^2\begin{cases} (C^2H^5)^2 \\ OH \\ O \\ OC^2H^5 \end{cases} + \left.\begin{matrix} C^2H^5 \\ H \end{matrix}\right\} + Zn\left\{\begin{matrix} OH \\ OH \end{matrix}\right.$$

Leucic ether.

(In these latter formulæ zinc is considered as bivalent.)

1 Liebig's Annalen, cxxxiii, p. 80.

2 Ibid, cxxxv, p. 34.

These reactions explain the formation of the leucic ether from oxalic ether and zinc ethyl, the two phases of the reaction being expressed more properly as follows:

$$C^2\begin{cases} O \\ OC^2H^5 \\ O \\ OC^2H^5 \end{cases} + 2Zn\begin{cases} C^2H^5 \\ C^2H^5 \end{cases} = C^2\begin{cases} (C^2H^5)^2 \\ OZnC^2H^5 \\ O \\ OC^2H^5 \end{cases} + Zn\begin{cases} C^2H^5 \\ OC^2H^5 \end{cases}$$

Oxalic ether. Zinco-monethyl-leucic ether. Zinco-ethylo-ethylate.

$$C^2\begin{cases} (C^2H^5)^2 \\ OZnC^2H^5 \\ O \\ OC^2H^5 \end{cases} + 2H^2O = C^2\begin{cases} (C^2H^5)^2 \\ OH \\ O \\ OC^2H^5 \end{cases} + Zn\begin{cases} OH \\ OH \end{cases} + \begin{matrix} C^2H^5 \\ H \end{matrix}\Big\}$$

Zinc-monethyl-leucic ether. Leucic ether. Zinc hydroxide.

The existence of the zinc-ethyloethylate was proved by Frankland,[1] in a previous investigation, having been obtained as intermediate product, by conducting oxygen into zinc ethyl, which was decomposed by water into zinc hydroxide and ethane.

This leucic ether of Frankland and Duppa was afterwards made the subject of investigation by Geuther and Wackenroder,[2] and proved not to be identical, but only isomeric with the leucic ether prepared from leucine. Salts of the acid obtained from leucine were described by Waage[3] and Thudichum,[4] and those of the isomeric acid by Frankland[5] and Wackenroder,[6] and found to be

1 Liebig's Annalen, xcv, p 42.

2 Jena'sche Zeitschrift iii, p. 341; also Zeitschrift für Chemie, N. F. iii, p. 709.

3 Liebig's Annalen, cxviii, p. 299.

4 Chemisches Centralblatt, 1862, p. 758.

5 Philosophical Transactions, 156 P. I. 317.

6 Jena'sche Zeitschrift, iii, p. 421.

quite different from one another, the non-identity of the two acids thus being proved beyond a doubt.

Geuther and Wackenroder also made comparative experiments on other isomeric ethers of the same empirical formula, but without obtaining positive results as to the true constitution of the leucic ether.

The same substance, leucic ether, or diethyloxalic ether, as it was afterward named by Frankland and Duppa, was obtained by L. Henry[1] in a different way. In the hope obtaining the ether, either of a ketone-acid, or of a tertiary alcohol acid, he allowed the chloride of ethyloxalic acid to act upon zinc ethyl. The reactions which could take place he expressed as follows:

$$\left[\begin{matrix}CO—Cl\\ |\\ CO—C^2H^5O\end{matrix}\right]^2 + Zn\left\{\begin{matrix}C^2H^5\\ C^2H^5\end{matrix}\right. = \left[\begin{matrix}CO—C^2H^5\\ |\\ CO—C^2H^5O\end{matrix}\right]^2 + ZnCl^2$$

and

$$\left[\begin{matrix}CO—Cl\\ |\\ CO—C^2H^5O\end{matrix}\right]^2 + 2Zn(C^2H^5)^2 = \left[\begin{matrix}OH\\ |\\ C=(C^2H^5)^2\\ |\\ CO—C^2H^5O\end{matrix}\right]^2$$

$$+ ZnCl^2 + Zn\left\{\begin{matrix}OH\\ OH\end{matrix}\right.$$

On treating the product of the reaction with water, the same substance was obtained which Frankland and Duppa had previously prepared, showing that the reaction took place according to the second of the above formulæ. The boiling point, 175°C., agreed with that found by Frankland and Duppa, and the vapor density, determined by Hofmann's method, was found to be 5.36; the

1 Berliner Berichte v, p. 949.

thereotical is 5.52. The two substances agree in all respects, and are in fact one and the same. It is the ethylic ether of oxalic acid in which an oxygen atom is replaced by two univalent ethyl groups, being the ether of a monobasic acid, the diethoxalic acid, and at the same time can be considered as a tertiary alcohol, since it contains the trivalent group $\equiv C\,O\,H$.

On heating this diethoxalic ether in sealed tubes with concentrated, fuming hydrochloric acid, at a temperature of 100°–110°C it undergoes decomposition, the free diethoxalic acid being formed. If, however, the temperature is raised to 130°– 150°C, and maintained at this point for 8–10 hours, the acid itself undergoes decomposition, the elements of water being eliminated, and an acid of the formula $C^6H^{10}O^2$ is formed, which was named ethocrotonic acid by Frankland and Duppa. As secondary products propion and ethyl chloride are formed, as proved by Geuther and Wackenroder.[1]

The ethylic ether of the ethocrotonic acid is also formed by treating the diethoxalic ether with phosphorus trichloride, as follows:[2]

$$3\left\{\begin{array}{l} C^2H^5 \\ | \\ C < \begin{array}{l} OH \\ CO\text{–}OC^2H^5 \end{array} \\ | \\ C^2H^5 \end{array}\right. + PCl^3 = \begin{array}{l} CH^3 \\ | \\ CH \\ \| \\ C\text{–}CO.OC^2H^5 \\ | \\ C^2H^5 \end{array} + P(OH)^3 + 3HCl$$

On treating this ether with potassium hydrate, it is decomposed, and the potassium salt formed, from which the free acid is easily obtained by acidifying with dilute

1 Zeitschrift für Chemie N. F. iii, p. 709.

2 Liebig's Annalen, cxxxvi, p. 2.

sulphuric acid and distilling, as the ethocrotonic acid distills readily with water vapor.

The ethocrotonic acid was prepared by Waldschmidt[1], by the dry distillation of *a* ethyl- *b* oxybutyric acid, water being eliminated as follows:

$$\begin{array}{l} CH^3 \\ | \\ CHOH \\ | \\ CHC^2H^5 \\ | \\ CO.OH \end{array} = \begin{array}{l} CH^3 \\ | \\ CH \\ \| \\ C.C^2H^5 \\ | \\ CO.OH \end{array} + H^2O$$

The properties of the free acid, and of the salts, corresponded with those given by Frankland and Duppa, so that there can exist no doubt as to the identity of the two acids.

Frankland and Duppa[2] found that on treating with potassium hydrate at 180°C., the ethocrotonic acid is decomposed, yielding acetic and butyric acids, but which of the two butyric acids is formed, is not stated. This point was afterwards settled by Petrieff,[3] who repeated the experiment of Frankland and Duppa, and found that normal butyric acid and acetic acid are formed on fusion with potassium hydrate, which corresponds with the behavior of the homologous acids of the same series toward this reagent.

1 Liebig's Annalen, clxxxviii, p. 245.
2 Ibid, cxxxvi, p. 7.
3 Berliner Berichte, vi, p. 1098.

Preparation of the Diethoxalic Ether.

The ethocrotonic acid, which served as material for the following investigations, was prepared according to the directions of Frankland and Duppa. Oxalic ether and ethylic iodide were mixed in proportion of one molecule of the former to two of the latter, and then so much metallic zinc added that it was just covered by the fluid. For this purpose granulated zinc was used, which had been previously very slightly amalgamated by immersion in a dilute solution of mercuric chloride. If the zinc is too strongly amalgamated, the reaction does not take place nearly as readily. The flask was then connected with a reversed condenser and kept at a temperature of 60°–70°C., in the water-bath, for 12–15 hours. At the end of this time the entire fluid had solidified to a yellowish, tenacious, semi-crystalline mass, to which, when cold, about three times as much water was added as the original volume of fluid. The mass was decomposed immediately on contact with water, gas being evolved in considerable quantity. As soon as the entire mass was completely permeated with water, it was distilled out of the same flask, and the distillation continued till no more oil was to be seen in the aqueous distillate. A saturated solution of sodium chloride was then added to the distillate, in order to aid the separation of the diethoxalic ether, which possessed nearly the same specific gravity as the aqueous portion. The distillate was thus divided into three layers, the lower of which was ethylic iodide,

which when separated from the others and dried over calcium chloride, was distilled, but proved to contain very little diethoxalic ether. The upper layer was decanted and brought over calcium chloride, which however dissolved in the ether in large quantities, till the whole mass assumed a pasty consistency. It apparently formed a compound with the ether which prevented its use as a drying agent. Accordingly water was added till the calcium chloride was completely dissolved, the ether then removed with the pipette and directly distilled without drying. The aqueous portion of the original distillate was extracted with ether, and so a small amount of diethoxalic ether obtained, which was added to the other portion, and the whole distilled together. At 100°C., the small amount of water which was still present in the ether, distilled over, and then the mercury rose rapidly to 170°C. and then gradually to 190°C. Above this temperature a small amount of substance distilled over, of an extremely penetrating and irritating odor, but it gave no constant boiling point, and the quantity was too small to undertake to determine its nature. The portion distilling between 170° and 190° was subjected once more to fractional distillation, when nearly the entire amount distilled at 170°–180°C., and this portion was employed for the preparation of the ethocrotonic acid, without further purification.

Preparation of the Ethocrotonic Acid.

The ethocrotonic acid was first prepared from the diethoxalic ether, according to the method of Geuther and Wackenroder,[1] by treating with concentrated hydrochloric acid. The diethoxalic ether was heated in portions of 10–15 grammes, with the three-fold volume of concentrated, fuming, hydrochloric acid, in sealed tubes, at a temperature of 130°–150° C. for 8–10 hours. At the end of this time the reaction seemed to be completed, and on the surface of the fluid in the tube was a dark brown layer of fluid of nearly the same volume as the diethoxalic ether employed, and the hydrochloric acid showed a strong greenish fluorescence.

On opening the tubes a considerable pressure was found. The upper layer was drawn off with a pipette, and the hydrochloric acid diluted and extracted with ether, and thus a considerable quantity of ethocrotonic acid recovered, which was dissolved in the hydrochloric acid. The brownish oil, together with the residue from the ethereal extract, was neutralized with sodium hydrate, nearly the whole going into solution, only a small portion remaining undissolved.

The alkaline fluid was then distilled till no more oil went over with the water vapor. This oil, according to the investigations of Geuther and Wackenroder, was probably propion, but the quantity obtained was relatively very small, and it was not further examined. The

1 Zeitschrift für Chemie, N. F. 111, p. 709.

fluid remaining in the flask after distillation was filtered, to remove a small amount of a brownish oily residue, which was not volatile, and then acidified with dilute sulphuric acid, and again distilled. The ethocrotonic acid distilled at once with the water vapor, as oil, but soon solidified in the receiver and also in the condenser. The distillation was continued till the distillate no longer gave an acid reaction with litmus. The crystalline mass of ethocrotonic acid was filtered off, dried between blotting paper, and then allowed to stand 24 hours in the desiccator over sulphuric acid. The filtrate was neutralized with calcium carbonate, and evaporated till a separation of the calcium salt began to take place on the water-bath. On cooling, the calcium ethocrotonate crystallized in brilliant, long needles, which were filtered off, and decomposed with hydrochloric acid, in order to obtain the free acid, which separated first as oil, but solidified almost immediately.

After the distillation of the ethocrotonic acid with water vapor, a considerable quantity of an easily soluble acid remained in the retort, which crystallized readily, and melted at 79°C., thus proving to be undecomposed diethoxalic acid. The entire residue was therefore extracted with ether, and thus a portion of diethoxalic acid recovered, nearly equal in quantity to the ethocrotonic acid obtained. It was, however, again treated with concentrated hydrochloric acid, and so converted into ethocrotonic acid.

In a second experiment, the ethocrotonic acid was prepared according to the method of Frankland and Duppa,[1]

1 Liebig's Annalen, cxxxvi, p. 2.

by treating the diethoxalic ether with phosphorus trichloride. The mixture of the two substances, in the proportion of three molecules of the former to one molecule of the latter, was heated gradually in the water bath, till the evolution of hydrochloric acid gas had ceased. The ethocrotonic ether was not isolated, but was directly saponified, the entire mixture being treated with potassium hydrate in excess. The flask was then connected with a reversed condenser, and heated in the water bath for seven hours; sulphuric acid was then added in excess, and the ethocrotonic acid distilled as before. The two methods give about the same yield, in both cases a considerable quantity of diethoxalic acid remaining undecomposed. The latter method, however, has the advantage that larger quantities can be operated upon at one time.

The ethocrotonic acid so prepared forms long, flat, colorless crystals, which are seldom regularly developed, owing to the rapid solidification of the acid. It melts at 41°C., and boils at 209°C., but sublimes gradually at ordinary temperatures, and has a rather sharp, penetrating odor. It is readily soluble in alcohol and ether, but sparingly so in water. Its solution reacts strongly acid, and neutralizes the strongest bases. The acid corresponds in all respects with that described by Frankland and Duppa.

Behavior toward Nascent Hydrogen.

One gramme of the pure acid was treated with five times the theoretical amount of four per cent. sodium amalgam. As soon as the fluid assumed an alkaline reaction, the flask was placed on the water-bath, and the sodium amalgam gradually added. It was kept at the temperature of boiling water till the evolution of hydrogen had entirely ceased, then filtered from the mercury, acidified with sulphuric acid, and distilled. The oil which at once distilled over with the water vapor, solidified in the condenser, and when dried, gave the melting point 41°C., and was accordingly unaltered ethocrotonic acid. The amount obtained was nearly equal to that employed in the first place.

By this experiment it is proved that hydrogen *in statu nascendi*, does not unite with the ethocrotonic acid, to form the corresponding caproic acid $C^6H^{12}O^2$, and that, in this respect the ethocrotonic acid shows the same behavior as the isomeric pyroterebic and hydrosorbic acids, and also as the angelic, crotonic and isocrotonic acids.

Behavior toward Hydrobromic Acid.

Ten grammes ethocrotonic acid were dissolved in concentrated, fuming, hydrobromic acid (saturated at 0°C.) This required a considerable quantity, about 200 c. c., as the ethocrotonic acid proved not to be very readily soluble in hydrobromic acid. The mixture was well agitated till complete solution had taken place, and then allowed to stand in a cool place. After the lapse of 12 hours, large, broad, crystals were formed on the surface, which when removed and dried, melted at 38°—39°C., proving to be mostly unaltered ethocrotonic acid. They were therefore redissolved in hydrobromic acid, and the solution allowed to stand several days at the ordinary temperature of the room. In two days a reddish oil was observed on the surface, which gradually increased in quantity. A portion of this oil was removed, washed with a small amount of water, and dried over sulphuric acid. It solidified in the desiccator, but on determining the melting point, was again found to be a mixture of unaltered acid and hydrobromic addition product. The acid was then allowed to stand for two months in contact with hydro bromic acid, at the end of which time it still remained liquid, but, however, on immersing the cylinder in ice, it solidified to a crystalline mass, which was filtered off, and dried over sulphuric acid and potassium hydrate. The melting point was found at 25°C., and in contact with water of the ordinary temperature it became fluid,

but solidified again under water at 0° C. A bromine estimation gave the following result:

0.2446 gr. decomposed with sodium amalgam gave
0.2353 gr. Ag_4Br. = 0.10013 gr. Br.
which is equal to 40.94 Br.
$C^6H^{11}Br^2O$ require 41.02 Br.

The absence of unaltered ethocrotonic acid was thus proved, and the substance was then decomposed with sodium amalgam.

Decomposition of the Hydrobromic Addition Product with Sodium Amalgam

Twenty grammes of this product were treated with three times the theoretical amount of four per cent. sodium amalgam. The flasks containing the substance, (in each about 10 grammes, with about 100 to 150 c c. water,) were placed in cold water, to avoid increase in temperature, and the sodium amalgam added in small portions at a time. From time to time a few drops of sulphuric acid were added, so that the fluid possessed only a slightly alkaline reaction, in order to avoid any further action on the compound by the sodium hydrate formed. As soon as the entire amount of sodium amalgam was consumed, and the evolution of hydrogen had ceased, which toward the end of the process became very copious, showing that no further reaction took place, the fluid was filtered from the residual mercury, acidified with sulphuric acid and distilled. At first, an oil was observed floating

on the surface of the water in the receiver, but as the quantity of water increased, it gradually dissolved. As soon as the distillate ceased to give an acid reaction, it was neutralized with calcium carbonate, the excess of the latter filtered off, and the filtrate evaporated on the water-bath till the calcium salt began to separate out. On cooling, however, it redissolved in the fluid, the salt being more soluble in cold than in hot water. It separated out in thin, lustrous lamellæ. The solution, when allowed to evaporate slowly in the desiccator, deposited small, transparent crystals, which, however, after removal from the mother liquor, became gradually opaque on remaining longer in the desiccator, evidently owing to the loss of water of crystallization. The calcium caproate was therefore simply allowed to dry, exposed to the air for a day or two, and then analysed.

0.2101 gr. of the air dried salt gave at 100° – 110°C.
0.0130 gr. H^2O, and 0.0999 gr. $CaSO^4$ = 0.0294 gr. Ca.

This corresponds to - - -	13.99 Ca.
and - - - - - -	6.19 H^2O.
$(C^6H^{11}O^2)^2Ca + H^2O$ requires -	13.89 Ca.
	6.25 H^2O.
	79.86 $C^6H^{11}O^2$.
	100.00

The salt has accordingly one molecule of water of crystallization.

The solubility in water was also determined with the following result:

6.4526 gr. of a solution which had stood in the desic-

cator till crystallization took place, accordingly saturated at 26.5°C. gave 0.5213 gr. $CaSO^4$ equal to 1.0349 gr. $(C^6H^{11}O^2)^2$ Ca. Therefore, in 100 parts of a solution saturated at 26.5°C., 16 parts of $(C^6H^{11}O^2)^2$ Ca are contained.

The purity of the acid being thus proved by the analysis of the calcium salt, the acid was liberated by means of hydrochloric acid, removed with the pipette, dried over calcium chloride and distilled. Almost the entire amount boiled at 194° – 195°C. (the mercury was completely enveloped in vapor.) In a freezing mixture, at a temperature of –15°C. it remained perfectly fluid and showed no viscidity. It is a colorless fluid, of a not unpleasant odor, is lighter than water, and not very readily soluble therein.

A combustion of the acid with oxide of copper gave the following result:

0.1943 gr. acid gave 0.4422 gr. CO^2 and 0.1780 gr. H^2O, equal to 0.1206 gr. C, and 0.0198 gr. H, corresponding

to	62.06 C.	C^6	= 72	= 62.07 C.
	10.19 H.	H^{12}	= 12	= 10.34 H.
		O^2	= 32	= 27.59 O.
			116	100.00

The barium salt was prepared from a portion of the acid, by neutralizing with barium carbonate. The solution was evaporated to a small volume, and allowed to stand in the desiccator, when it became syrupy, before the least crystallization took place. At first a crystalline crust was formed on the surface, and then larger crystals were gradually formed underneath the crust. These lat-

ter were removed, avoiding as much as possible an admixture with the fragments of the crust, allowed to dry a few days in the air, and then analyzed.

0.2337 gr. Ba salt gave 0.0215 gr. H^2O,
and 0.1366 gr. $BaSO^4$ = 0.0802 gr. Ba.
This corresponds to - 34.33 Ba.
and - - - - 9.18 H^2O.
$(C^6H^{11}O^2)^2Ba+2H^2O$ requires 33.99 Ba.
8.93 H^2O.
57.08 $C^6H^{11}O^2$

100.00

The barium salt has accordingly two molecules of water of crystallization.

From another portion of the acid the ethylic ether was prepared. For this purpose it was mixed with about the double volume of absolute alcohol, and an equal volume of concentrated sulphuric acid, and the mixture gently warmed for half an hour in the water-bath. On the addition of water, the ether separated on the surface of the fluid, and was removed with the pipette, washed with a few drops of sodium carbonate to remove free acid, then with water, and finally brought over calcium chloride. It distilled completely at 151.5° C. It formed a colorless, mobile liquid, lighter than water, of a peculiar, rather pleasant odor, faintly resembling that of peppermint.

The combustion with copper oxide gave the following result:

0.1970 gr. ether gave 0.4807 gr. CO^2, and 0.1945 gr. H^2O, equal to 0.1311 gr. C., and 0.0216 gr. H, which corresponds to

66.55 C.	C^8	= 96 =	66.66 C.
10.97 H.	H^{16}	= 16 =	11.11 H.
	O^2	= 32 =	22.23 O.
		144	100.00

The characteristic properties of the acid and its compounds leave no room for doubt but that the caproic acid obtained from the hydrobromic addition product of the ethocrotonic acid is the diethacetic acid.

The boiling point of the acid was found at 190°C., by Saytzeff,[1] who obtained the diethacetic acid from the diethyl carbinol, by means of the cyanogen compound, but on the other hand Schnapp,[2] who obtained the same acid by heating the *a* diethyl *b* oxybutyric acid, according to the following equation:

$$\begin{array}{l} CH^3 \\ | \\ CHOH \\ | \\ C(C^2H^5)^2 \\ | \\ CO.OH \end{array} = \begin{array}{l} CH^3 \\ | \\ CHO \\ | \\ CH(C^2H^5)^2 \\ | \\ CO.OH \end{array}$$

gives the boiling point at 195 – 197° C.

The boiling point of the ethylic ether of the acid coincides with that observed by Frankland and Duppa[3], who obtained the ether by the successive action of metallic sodium and ethylic iodide on acetic ether. The ether

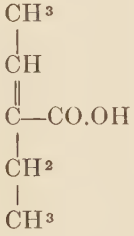
1 Liebig's Annalen, xcciii, p. 349.

2 Berliner Berichte, x, p. 1953.

3 Liebig's Annalen, cxxxviii, p. 218.

thus obtained boiled at 151°C., and that prepared by Saytzeff had also the same boiling point, so that notwithstanding the slight variations in the behavior of the calcium and barium salts, and in the boiling point of the free acid, as given above, and the observations of other investigators, there can be no doubt as to the identity of the acid thus obtained from the ethocrotonic acid with the diethacetic acid.

The constitution of the ethocrotonic acid is thus proved to be as follows:



Decomposition of the Monobromdiethacetic Acid with Sodium Carbonate.

Four grammes were treated in a sealed glass tube with sodium carbonate in excess, and allowed to stand at the ordinary temperature. The fluid soon became turbid, even before complete solution took place, owing to the separation of an oily substance, which floated on the surface of the fluid. After the lapse of 24 hours the evolution of gas had ceased, and a considerable amount of oil had collected on the surface. On opening the tube a strong pressure was found, due to carbonic acid. The oil

was removed with the pipette, washed with water, and dried over calcium chloride. In order to obtain larger quantities of this substance, 14 gr. monobromdiethacetic acid were treated in a small flask with sodium carbonate in proportion of equal molecules and about 100–150 c. c. water. The flask was connected with a reversed condenser, placed in ice water, and kept at this temperature till the evolution of carbonic acid had ceased. When no further reaction was to be seen, the flask was connected with a condenser in which ice water circulated, and the receiver was also placed in ice, as the substance was found to be extremely volatile. The water bath was then gently warmed, when the oil easily distilled over, almost entirely free from water. It was brought over calcium chloride, with the previous portion, and when dry was distilled; it boiled at 37–39°C., a small amount remaining in the retort, which boiled above 160°C., and was probably due to a polymerisation. To the distillate, bromine was added, drop by drop, till the color of the latter no longer disappeared. The bromine was absorbed with great avidity, at first every drop producing a slight hissing sound. The fluid was then washed with sodium carbonate and water, dried over calcium chloride, and the bromine determined.

0.1898 gr. gave 0.3111 gr. Ag Br. = 0.1323 gr. Br.

equal to - - 69.72 Br.

$C^2H^{10}Br^2$ requires 69.56 Br.

The remainder of the substance was distilled, and the boiling point found at 178-180°C. A slight decomposition took place, traces of hydrobromic acid being liberated

and a minute amount of fluid remaining in the retort, which boiled above 180°C. According to these properties, the substance was ethylpropylene,

$$CH^3—CH^2—CH = CH—CH^3$$

Wischnegradsky,[1] in his investigations on the amylenes and amyl alcohol, found in the commercial amylene, two isomeric hydrocarbons, trimethylethylene, and unsymmetrical methylethylethylene, which he found to be soluble in sulphuric acid, and whose constitution was proved by means of the alcohols thus prepared with the aid of sulphuric acid. Besides this soluble portion he obtained an insoluble amylene, mixed with amylhydride, which was not separated, and consequently the boiling point not determined. This amylene was treated with bromine, and the resulting compound found to boil between 170° and 180° C. It was next converted into the iodide, and then into the alcohol, which was proved to be methylpropylcarbinol,

$$CH^3—CH^2—CH^2—CH<\begin{matrix}OH\\CH^3\end{matrix}$$

and consequently the amylene from which it was formed must have been constituted according to one of the following formulæ:

$$CH^3—CH^2—CH^2—CH=CH^2,$$

or $$CH^3—CH^2—CH=CH—CH^3.$$

The first of these could only be formed from the normal amyl alcohol, the second either from ethylpropylcarbinol or from diethylcarbinol. Wischengradsky was inclined

1 Liebig's Annalen, cxc, p. 328.

to assume the presence of the former, and consequently the presence of normal amyl alcohol in the alcohol from which the amylene was originally prepared. A comparison of the boiling points of the bromide of the amylene obtained from the monobromdiethacetic acid, and that from the commercial amylene as given by Wischnegradsky would point to the probable identity of the hydrocarbons, and to the constitution

$$CH^3—CH^2—CH=CH—CH^3,$$

as it is scarcely to be assumed that a substance of the constitution

$$CH^3—CH^2—CH^2—CH=CH^2$$

would be formed from

$$\begin{matrix} CH^3—CH^2 \\ CH^3—CH \end{matrix} > CBr—CO.OH$$

Out of the iodide of fermentation amyl alcohol, two amylenes were obtained, unsymmetrical methylethylethylene, and isopropylethylene, which latter boils at 21.5°C. The only one of all these hydrocarbons which boils above 30°C. is the trimethylethylene

$$\begin{matrix} CH^3 \\ CH^3 \end{matrix} > C=CH—CH^3$$

which boils at 36°C, but the formation of such a substance from the monobromdiethacetic acid would be entirely unintelligible, without the assumption of intermolecular changes, by which the group

$$CH^3 — CH^2 — CH =$$

would be converted into the group

$$\begin{matrix} CH^3 \\ CH^3 \end{matrix} > C =$$

but since the formation of the amylene took place at a temperature below 40°C. there is no reason whatever for such an assumption, and the amylene obtained has without doubt the composition of the ethylpropylene

$$CH^3 - CH^2 - CH = CH - CH^3$$

The alkaline fluid remaining from the distillation of the amylene, was acidified with sulphuric acid and distilled. A small amount of a volatile acid distilled over with the water vapor, and was converted into the calcium salt, which was then decomposed with hydrochloric acid. The acid thus liberated crystallized at once, and the melting point was found at 41°C., thus proving to be a small amount of ethocrotonic acid which had been regenerated by the action of the sodium carbonate. The fluid remaining in the retort after the distillation of the ethocrotonic acid, was extracted with ether, and thus a small quantity of a non-volatile acid obtained, which on standing in the desiccator formed a thick, gummy mass, but could not be brought to crystallization. The calcium salt of this acid was extremely soluble in water and alcohol, but could also only be obtained as a thick, viscid mass. With copper acetate it gave a precipitate on boiling, which was filtered off, suspended in water, and decomposed with hydrogen sulphide, in the hope of obtaining the free acid in a pure state. On concentrating the filtrate, however, it again formed a thick syrup. Even when placed in a freezing mixture and cooled to –30°C., it did not crystal-

lize, but simply became more viscid. The same acid was afterwards obtained by the decomposition of the monobromdiethacetic acid with water, in slightly greater quantity.

The chief reaction taking place by the decomposition of the monobromdiethacetic acid with sodium carbonate, is the formation of hydrocarbon, amylene. The acid is first neutralized by the sodium carbonate, but the sodium salt is decomposed, even at the ordinary temperature, in consequence of the affinity of the bromine to the sodium atom contained in the same molecule. Sodium bromide is eliminated, and by this means one affinity of the oxygen atom of the carboxyl group is set free, which releases the carbon atom from the rest of the molecule, forming CO^2.

$$\begin{matrix} CH^3\text{–}CH^2 \\ CH^3\text{–}CH^2 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} Br \\ CO.O\ Na \end{matrix} = \begin{matrix} CH^3\text{–}CH^2 \\ CH^3\text{–}CH^2 \end{matrix}\!\!>\!C\!=\!+\ NaBr + CO^2$$

The hydrocarbon thus formed should have the above constitution, but proved to be identical with ethplpropylene, which has in all probability the constitution

$$CH^3 - CH^2 - CH{=}CH - CH^3$$

If the latter is correct, one hydrogen atom must pass from one carbon atom to the next, at the moment of liberation of the amylene, in a manner similar to that observed by the action of sodium upon $CH^3 - CHCl^2$, and upon $CH^2Br - CH^2 - CH^2Br$, where, instead of the hydrocarbons $CH^3 - CH{=}$ and $-CH^2 - CH^2 - CH^2-$ the hydrocarbons $CH^3{=}CH^3$ and $CH^3 - CH{=}CH^2$ are obtained.

The regeneration of the ethocrotonic acid is explained

by the simple elimination of the elements of hydrobromic acid. The formation of the oxy-acid is due to the action of the water, hydrobromic acid being eliminated and hydroxyl replacing the bromine atom in the molecule without any further decomposition.

$$\begin{matrix}CH^3\text{–}CH^2\\CH^3\text{–}CH^2\end{matrix}>C<\begin{matrix}Br\\COOH\end{matrix}+H^2O=\begin{matrix}C^2H^5\\C^2H^5\end{matrix}>C<\begin{matrix}OH\\CO.OH\end{matrix}+HBr$$

These latter reactions take place only to a small extent, the chief reaction being the formation of amylene.

Decomposition of the Monobromdiethacetic Acid with Water.

18 grammes were treated with five times the weight of water, in sealed tubes, immersed in boiling water for 20–24 hours. At the end of this time decomposition was complete, and on the surface of the water was a layer of oil nearly equal to the amount of substance employed. On opening the tubes a considerable pressure was found, and carbonic acid gas escaped. The oil was removed with the pipette, and washed with dilute sodium hydrate to remove free acid. By this operation a large proportion of the fluid went into solution, only about one-fourth of the original volume remaining undissolved. This was washed with water, dried over calcium chloride, and the boiling point determined. This was found at 37°C. The fluid was therefore the same as was obtained by the decomposition with sodium carbonate, namely ethylpropylene. The alkaline solution was added to the por-

tion remaining in the tubes, the whole acidified and distilled as long as the distillate continued to react acid. The distillate was then neutralized with calcium carbonate, and the acid liberated from the calcium salt thus obtained. It crystallized immediately, and gave the melting point 41° C.; was acordingly ethocrotonic acid. The fluid remaining in the retort after the distillation of the ethocrotonic acid was extracted with ether, and so a small portion of oxy-acid obtained From this the barium salt was prepared, but proved to be extremely soluble in water and alcohol, and it was impossible to obtain it well crystallized. It was accordingly evaporated to complete dryness, and then dissolved in hot, absolute alcohol, in which it was not so extremely soluble. On cooling, it separated in the form of a flocculent mass, which could, however, be recognized as consisting of minute needles; the whole mass presented a woolly appearance. It was filtered off, dried for a day in the desiccator, and then analysed.

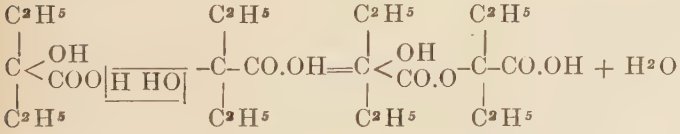
0.2592 gr. dried at 100° lost 0.0061 gr. H^2O, and gave
0.1470 gr. $BaSO^4$ = 0.0864 gr. Ba., corresponding to

34.15 Ba (1)	$(C^6H^{11}O^3)^2Ba + \frac{1}{2} H^2O$	
2.35 H^2O	require 34.33 Ba.	
	2.20 H^2O.	

1 Calculated for the anhydrous salt.

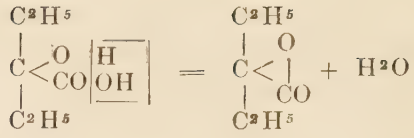
Although the loss of weight at 100° C., corresponds very closely with half a molecule of water of crystallization, the salt was probably anhydrous, the loss of weight being due to moisture still adhering to the mass. Another portion of the purified barium salt was decomposed

with dilute sulphuric acid, the least excess of the latter being carefully avoided. The filtrate from the barium sulphate was evaporated to a small bulk, and then placed in the desiccator, but formed only a thick syrup, which even in a freezing mixture did not crystallize. However, after long standing over sulphuric acid, it gradually solidified to a semi-crystalline mass. This was pressed betwen blotting paper and dissolved in a few drops of water, in which it was extremely soluble, and again placed in the desiccator. This time it crystallized more readily; a portion was removed, pressed between blotting paper and dried in the desiccator. The melting point was found at 48°–52°C. It was very deliquescent, so that it was difficult to bring it into the capillary tube, to determine the melting point, without its attracting moisture. The acid had apparently undergone some further decomposition, by evaporation, or on standing in the desiccator, analogous to that found by Wislicenus[1] for the lactic acid, namely the formation of an anhydride, or of a substance analogous to the lactide, caused by the elimination of the elements of water, either from two molecules, or from one molecule of the free acid, as follows:



or else

1 Liebig's Annalen, clxiv, p. 181.



The formation of a small amount of either of these substances could account for the difference in behavior of the acid obtained from monobromdiethacetic acid, and diethoxalic acid.

To another portion of the barium salt was added a concentrated solution of copper acetate, both solutions being first heated to boiling. A pulverulent precipitate was formed almost immediately, which increased on continued heating. This precipitate was decomposed with hydrogen sulphide in the same manner as with the oxyacid obtained by decomposition with sodium carbonate, but it was again found impossible to obtain the acid thus, in the solid state, as it again became thick and viscous in the desiccator. It was therefore converted into the barium salt, and then reprecipitated with copper acetate. The precipitate was filtered off, the filtrate giving a strongly acid reaction with litmus, well washed, dried at 100° C. and analysed. When dry it formed a very light, fine powder of a light blue color. The analysis gave the following results:

0.1212 gr. gave 0.0490 gr. CuO = 0.0388 Cu
0.1724 gr. gave 0.2359 gr. CO^2 and 0.0803 gr. H^2O,
corresponding to 0.0643 gr. C, and 0.0089 gr. H,
equal to - - - - - 32.21 Cu.
37.32 C.
5.17 H.

which corresponds to the formula $C^6H^{10}O^3Cu$

Cu	= 63.3	= 32.74 Cu.
C^6	= 72	= 37.25 C.
H^{10}	= 10	= 5.12 H.
O^3	= 48	= 24.89 O.
	193.3	100.00

The salt is accordingly basic, and has the following constitution :

$$\begin{matrix} C^2H^5 \\ C^2H^5 \end{matrix} > C < \begin{matrix} O\text{–}Cu \\ | \\ CO.O \end{matrix}$$

and its formation would be thus expressed :

$$(C^2H^5)^2C < \begin{matrix} OH \\ CO.O \end{matrix} > Ba + 2 \begin{matrix} CH^3\text{–}CO.O \\ CH^3\text{–}CO.O \end{matrix} > Cu =$$

$$(C^2H^5)^2C < \begin{matrix} CO.O \\ OH \end{matrix}$$

$$2(C^2H^5)^2C < \begin{matrix} O\text{–}Cu \\ | \\ CO.O \end{matrix} + \begin{matrix} CH^3\text{–}CO.O \\ CH^3\text{–}CO.O \end{matrix} > Ba + 2\ CH^3\text{–}CO.OH$$

In order to compare the behavior of pure diethoxalic acid under the same treatment, barium diethoxalate was prepared from a small portion of the acid obtained by the decomposition of the diethoxalic ether, for the preparation of the ethocrotonic acid. This was then treated with copper acetate in the same manner as before, but gave no precipitate. It was concentrated on the water bath to a small volume, and allowed to crystallize. The The cupric diethoxalate separated in compact round masses of a light blue color. The mother liquor was decanted, and the mass redissolved in a small amount of water; on heating, to aid solution, a copious precipitate

was formed, which presented exactly the same appearance as that obtained from the monobromdiethacetic acid, being of a fine, pulveralent character, and quite different from that which first crystallized out. The degree of concentration of the solution, or the presence or absence of other salts seem to favor or prevent the formation of this basic salt in some way not yet explained.

The quantity of oxy-acid, obtained by the decomposition of the monobromdiethacetic acid, was too small to demonstrate its nature with positive certainty, but there can hardly exist any doubt as to its being diethoxalic acid, in view of the analyses and characteristics above given.

The same decomposition products are therefore obtained on treating the monobromdiethacetic acid with water as with sodium carbonate, simply the relative amounts being different. When water is employed, the chief product is regenerated ethocrotonic acid, the hydrocarbon is formed in much smaller quantity than with sodium carbonate, and the oxy-acid in slightly greater amount, than by the other method, but still, in proportion to the amount of material employed, the quantity obtained is very small.

Behavior of the Ethocrotonic Acid toward Bromine.

15 grammes ethocrotonic acid were dissolved in purified carbon-disulphide, in which it was readily soluble, and to the solution the theoretical amount of bromine, (1 molecule of Br^2 to 1 molecule $C^6H^{10}O^2$) gradually added, the cylinder containing the fluid being placed in cold water to avoid increase of temperature. The bromine was absorbed with avidity, as shown by the immediate decolorization; at the end of the operation, however, a slight permanent coloration remained. During the operation, only the slightest traces of hydrobromic acid were evolved, showing that no substitution took place, but simply addition. The carbon disulphide was allowed to evaporate, and the mass re-crystallized from the same solvent. It crystallized readily in well formed crystals, and gave the melting point 80.5°C. A bromine estimation gave the following result:

0.2209 gr. gave 0.3018 gr. Ag Br. =
0.1284 gr. Br. corresponding to 58.12 Br.
$C^6H^{10}Br^2O^2$ require 58.39 Br.

The dibromdiethacetic acid was thus proved to be pure.

Decomposition of the Dibromdiethacetic Acid with Sodium Carbonate.

12 grammes were treated with sodium carbonate in excess, in a small flask, which was connected with a reversed condenser and placed in a cold water-bath. The fluid soon became turbid, even before solution had taken place, owing to the separation of an oil which collected gradually at the bottom of the flask.

The water-bath was gently warmed till no more evolution of carbonic acid was to be seen. The flask was then removed, and the oil distilled with the water vapor. It was readily volatile, the first portions of the distillate consisting almost entirely of oil. This was separated from the aqueous portion of the distillate, dried over calcium chloride and distilled. It began to boil at 108–110°, but the main portion distilled at 110–112° and 112–115°, from 115–120° a small amount distilled over, and then the mercury rose rapidly to 175°, but gave no constant boiling point. The largest portion boiled at 110–112° C., and of this a bromine estimation was made.

0.2279 gr. ignited with caustic lime gave
0.2579 gr. Ag Br.=0.1097 gr. Br.
this corresponds to 48.18 Br.
C^5H^9Br require 53.69 Br.

Thinking perhaps the deficiency might be due to the presence of a small quantity of water, it was again treated with calcium chloride and re-distilled, but it again

gave no constant boiling point, and a second bromine estimation gave the following result:

0.1896 gr. ignited with caustic lime gave
0.2307 gr. Ag Br = 0.0982 gr. Br.
which corresponds to 51.80 Br.
C^5H^9Br require 53.69 Br.

The substance on standing, even in well corked tubes, gradually assumed a yellow color.

There can be but little doubt but that the substance was bromamylene of the above formula, but it apparently was readily decomposed or oxidized, in a manner perhaps analagous to the oxidation of bromethylene observed by Demole,[1] who also experimented upon bromamylene, which was, however, found not to be oxidized by exposure to free oxygen. It is not stated which amylene was experimented upon, but in all probability it was obtained from the commercial variety, and as the conditions of the experiment were entirely different, it is uncertain whether the brom-ethylpropylene does not undergo, at least, a partial oxidation.

The alkaline fluid from which the bromamylene was distilled was acidified and again distilled. The aqueous distillate gave an acid reaction, and was therefore neutralized with calcium carbonate. The acid was liberated from the calcium salt thus obtained, with hydrochloric acid, and the melting point found at 41°C., thus proving to be regenerated ethocrotonic acid, but the amount was extremely small.

The residue remaining in the retort after the distilla-

1 Berliner Berichte, xi, p. 1302.

tion of the ethocrotonic acid was evaporated to a small volume, and extracted with ether, and so a small amount of an oxy-acid obtained, which crystallized readily and was very soluble in water and alcohol, but less so in ether. The aqueous solution was purified by boiling with animal charcoal, evaporated to a small volume and allowed to stand in the desiccator. It soon formed minute transparent crystals, which gave the melting point 141°C., but the quantity was insufficient for an elementary analysis. The same acid was afterwards obtained in greater quantity by the decomposition of the dibromdiethacetic acid with water, and its constitution satisfactorily determined.

Decomposition of the Dibromdiethacetic Acid with Water.

20 grammes were treated, in portions of five grammes, with five times the weight of water, in sealed tubes, which were then immersed in boiling water 20–24 hours. At the end of this time the substance appeared to be completely decomposed, and a heavy oil had collected at the bottom of the tubes, which remained unaltered on further heating. On opening the tubes a considerable pressure was observed, and carbonic acid escaped. Thinking perhaps the decomposition of the bromamylene, indicated by the deficiency in the amount of bromine found in the previous experiment, might have been caused by the distillation with water vapor, the oil was

this time simply removed with the pipette, washed with sodium carbonate to remove free acid, and dried over calcium chloride, In order to avoid the possibility of a decomposition or polymerisation by the distillation, it was first analysed, as it appeared to be pure, being perfectly colorless.

0.3387 gr. ignited with caustic lime gave
0.3690 gr. Ag Br. = 0.1570 gr. Br.
this corresponds to 46.36 Br.
C^5H^9Br. requires 53.69 Br.

The fluid was then distilled, but without obtaining any constant boiling point. It began to distill at 108° as before, and the chief portions distilled from 110–113° and 113–116°. Above this point very little distilled, the mercury rising gradually to above 175°C., as in the previous experiment. Immediately after the distillation, the portions boiling at 110–113° and 113–116° were introduced into the weighing tubes and employed for analysis; by this means the possibility of the oxidation of the substance by exposure to the air, was this time excluded.

The first portion, with the boiling point 110–113°, gave the following result:

0.2694 gr. ignited with caustic lime gave
0.3022 gr. Ag Br. = 0.1281 gr. Br.
this corresponds to 47.55 Br.
C^5H^9Br require 53.69 Br.

The second portion, boiling at 113–116°, gave the following result:

0.2582 gr. ignited with caustic lime gave
0.2928 gr. Ag Br.= 0.1246 gr. Br.
this corresponds to 48.25 Br.
C^5H^9Br require 53.69 Br.

The bromamylene apparently undergoes some partial decomposition on continued heating with water, or else it contains a small amount of some other substance, formed perhaps in consequence of the regeneration of the ethocrotonic acid. A process analogous to that found by Demole,[1] by which the substance

$$\begin{array}{l} CHBr \\ \| \\ CHBr \end{array}$$

is transformed by the action of oxygen into

$$\begin{array}{l} CH^2Br \\ | \\ CBrO \end{array}$$

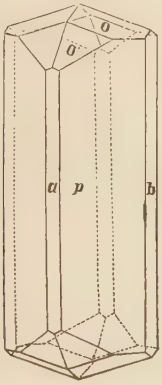
might perhaps have taken place.

A portion of that boiling at 110–113°C. was treated with bromine in the hope of obtaining a substance of the formula $C^5H^9Br.Br^2$. The bromine was at first absorbed, but almost immediately evolution of hydrobromic acid occurred, showing that a substitution instead of an addition took place. The fluid was placed in a freezing mixture, but no signs of solidification could be observed. Notwithstanding the fact that the substance contained less bromine than required by the formula C^5H^9Br, there can be little doubt but that the main portion of the same consisted of bromamylene.

1 Berliner Berichte, xi, p. 1307.

The aqueous portion, remaining after the removal of the bromamylene, was diluted somewhat and distilled, The distillate, which gave an acid reaction, was neutralized with calcium carbonate, and from the calcium salt a small amount of ethocrotonic acid obtained, which melted at 41°C.

The residue remaining in the retort was evaporated to a small volume, and extracted with ether, in order to obtain the oxy-acid. The ether took up only small quantities of the acid, and it was necessary to continue the operation for a long time, in order to extract the entire amount of oxy-acid. The acid crystallized readily from the ethereal residue, and when purified by boiling with animal charcoal, and gradually evaporated in the desiccator, formed small, transparent, needle-shaped crystals, with the melting point 141°C., which were found to belong to the rhombic system.



$$a : b : c = 0.9573 : 1 : 0.3328$$

The following forms were observed:

$p = \infty P$ (110)

$a = \infty \bar{P} \infty$ (100)

$b = \infty \breve{P} \infty$ (010)

$o = P$ (111)

$o' = \breve{P}\frac{1}{3}$ (311)

				Observed.	Calculated.
∞P : ∞P	= (110)	: $(1\bar{1}0)$	=	87°30′	——
P : P	= (111)	: $(1\bar{1}1)$	=	34°54′	——
P : P	= (111)	: $(\bar{1}11)$	=	36°	36°30′40″
$\breve{P}\frac{1}{3}$: $\breve{P}\frac{1}{3}$	= (311)	: $(3\bar{1}1)$	=	26°9′	25°56½′
$\breve{P}\frac{1}{3}$: $\breve{P}\frac{1}{3}$	= (311)	: $(\bar{3}11)$	=	88°36′	89°24′

The crystals usually form minute needles, elongated in the direction of the vertical axis, but are sometimes obtained in very short prisms, the pyramids almost uniting at the base. The two pinacoids, *a* and *b*, are very narrow, and often one or both are entirely wanting. On the needle-shaped crystals the pyramid $\breve{P}\frac{1}{3}$ is predominating; on the short prismatic crystals the two pyramids are nearly equally developed.

A combustion of the free acid with copper oxide gave the following result:

0.2033 gr. gave 0.3563 gr. CO^2 and 0.1462 gr. H^2O equal to 0.0972 gr. C and 0.0162 gr. H, which corresponds to 47.81 C. $C^6H^{12}O^4$ require 48.65 C.
7.97 H. 8.11 H.

The acid, however, proved to be not quite pure, as a very slight inorganic residue was left in the platinum boat after the combustion, which accounts for the deficiency in carbon and hydrogen. The acid was therefore recrystallized from ether, in order to remove all inorganic substance, and when thus purified, was again analyzed:

0.3524 gr. (dried at 100°,) gave 0.6270 gr. CO^2 and 0.2543 gr. H^2O = 0.6710 gr. C and 0.0283 gr. H.

this corresponds to - - - - 48.52 C.

and - - - - - - - - 8.03 H.

C^6 = 72 = 48.65 C.

H^{12} = 12 = 8.11 H.

O^4 = 64 = 43.24 O.

100.00

The acid has, therefore, the above composition.

It is very easily soluble in water and alcohol, less so in ether, and completely insoluble in carbon disulphide, benzene, chloroform and ligroïne. It does not volatalize at ordinary temperatures, but at 100°C. it loses weight very gradually.

The calcium salt was first prepared, but was found to be extremely soluble, and in the desiccator formed a thick, gummy mass. It was dissolved in alcohol, in which it was easily soluble, and ether was added to the solution. The salt was precipitated, but became almost immediately gummy and slimy, so that it was impossible to obtain the salt pure in this way.

The barium salt was found also to be so extremely soluble that it was impossible to obtain it in any other form than as a thick syrup. It was accordingly treated with a dilute solution of copper sulphate till no more barium sulphate was precipitated. The solution of the copper salt thus obtained was evaporated, during which operation it was found that on heating the solution to boiling, an apparently basic salt was separated as a fine powder of a light blue color, which when once separated,

was absolutely insoluble in water. This was filtered off, suspended in water and decomposed with hydrogen sulphide. The acid thus regained, crystallized easily, and melted at 141° C, thus proving to be the same as the original acid, and that the precipitate was not due to the presence of any foreign substance. The filtrate from the precipitate was then cautiously evaporated on the water-bath, the temperature being kept considerably below boiling, and thus the separation of the basic salt avoided. The solution thus concentrated, was placed over sulphuric acid in a vacuum, and allowed to stand. In a day or two crystals were formed, but there was also a small amount of the pulverulent precipitate intermixed, so that it was necessary to recrystallize. It was accordingly dissolved in alcohol, but on warming to aid solution, the precipitation of the basic salt again occurred, which was filtered off and the filtrate placed in the exhausted receiver. This easy precipitation of the basic salt would thus seem to be characteristic for the acid, but the quantity at disposal was too small to investigate this reaction further.

The alcoholic solution deposited at first on the edges a small amount of minute compact blue crystals, and then fine needles of a much lighter color, these latter forming by far the largest portion. It was apparently a mixture of two salts differing in the amount of water of crystallization, but the amount was much too small to attempt a separation, and the mixture was accordingly employed directly for the analysis.

0.1580 gr. of the air-dried salt gave at 120–130°C.
0.0238 gr. H^2O and 0.0298 gr. CuO=0.0238 gr. Cu,
this corresponds to - - - - 17.73 Cu.

$(C^6H^{11}O^4)^2Cu$ require 17.74 Cu.

0.0238 gr. H^2O = 15.06 H^2O.

$3\frac{1}{2}$ Mol. H^2O require 14.98 H^2O.

The true amount of water of crystallization is somewhat uncertain, owing to its being a mixture of two salts apparently.

The acid has accordingly the following constitution:

$$\begin{array}{l} C^2H^5 \\ | \\ C<\begin{array}{l}OH \\ CO.OH\end{array} \\ | \\ CHOH \\ | \\ CH^3 \end{array}$$

Its formation from the dibromdiethactic acid is easily explained by the elimination of the two bromine atoms in the form of hydrobromic acid, and the substitution of two hydroxyl groups in their place. It is accordingly a monobasic, triatomic acid, being a hitherto unknown member of the glyceric acid series, and therefore the name "hexeric acid" seemed appropriate as indicating its relation to the glyceric acid, and at the same time to the caproic or hexylic acids.

The reactions taking place in the decomposition of the dibromdiethacetic acid with water, are thus seen to be the same as those which occur on treating with sodium carbonate, the relative amounts of the various products only, being slightly different, more oxy-acid and less brominated hydrocarbon being formed when water is used than with sodium carbonate.

A summary of the results of the above described investigations is then as follows:

Ethocrotonic acid with nascent hyrogen gives no addition-product; with hydrobromic acid it gives a crystalline compound melting at 25°C., the monobromdiethacetic acid; this latter compound treated with nascent hydrogen gives diethacetic acid boiling at 194°–195°C. The monobromdiethacetic acid decomposed with sodium carbonate, or water, yields three products; a hydrocarbon, ethylpropylene, boiling at 37°–38°C; a small amount of regenerated ethocrotonic acid, and an oxy-acid, probably diethoxalic acid. Ethrocrotonic acid with bromine gives a crystalline compound, melting at 80.5°C., the diebromdiethacetic acid. This compound, decomposed with sodium carbonate, or water, yields also three products: a brominated hydrocarbon, bromamylene, boiling probably between 110° and 115°C., a small amount of regenerated ethocrotonic acid, and an oxy-acid melting at 141°C.- the hexeric acid.

All these reactions and decompositions are simply and naturally explained by the following structural formula for the ethocrotonic acid, and there can be no doubt but that it expresses the true constitution: